

15 BORON AND MOLYBDENUM

Boron and molybdenum are the two micronutrients that are taken up by plant as anions. However, their chemistry in soils is quite different, and therefore each nutrient is separately discussed.

15.1. BORON

The total concentration of boron in most soils varies between 2 and 200 mg kg⁻¹, and less than 5% is generally available to plants (Tisdale et al., 1985). Boron-containing minerals in soils are tourmaline, axenite, ulexite, colemanite, and kermite; tourmaline is the most important. Boron-containing minerals are quite resistant to weathering, and most plant-available B comes from the decomposition of soil organic matter and from B adsorbed and precipitated onto the surface of soil particles.

Boron is highly mobile in soils (in contrast to being highly immobile in plants). Consequently, both B deficiencies and toxicities are of concern. Soils of humid regions such as sandy podzols, vertisols, alluvial soils, and organic soils have low amounts of plant-available B due to leaching of B. Boron deficiencies have been reported from many countries having such soils, namely, the United States, Canada, England, New Zealand, India, and Nigeria (Gupta, 1985). In the United States some soils in the Atlantic coastal plain, the Pacific coastal area, the Pacific Northwest, and northern Michigan, Wisconsin, and Minnesota appear to be low in B.

Boron, like sodium and chloride, is soluble and tends to accumulate where salts accumulate. Thus B may be found in toxic levels in salinic and sodic soils, in low lying areas with impeded drainage, and in areas with a shallow water table. Irrigation water high in B content is a major cause of B toxicity. Overall in nature, B toxicity is not as widespread as B deficiency.

15.1.1. Forms of Boron in Soils

In addition to being present as a component of minerals and rocks, B exists as (1) adsorbed onto surfaces of clay minerals and hydroxides of Al

and Fe; (2) complexed with soil organic matter; and (3) in the soil solution as soluble B, either as free, nonionized H_3BO_3 or as ionized $\text{B}(\text{OH})_4^-$ forms.

1. Adsorbed B: There are three possible mechanisms for interlayer adsorption of B: (a) H bonding of $\text{B}(\text{OH})_3$ with the oxygen-rich interlayer of clay platelets; (b) borate ion ionically bound to materials adsorbed onto the interlayer surfaces (e.g., hydroxyl-Al material); and (c) interlayer material that could move out to external sites or into solution and then react with borate ions (Evans and Sparks, 1983). Thus Fe and Al, present as interlayer materials in various forms, seem necessary for B sorption on clays (Gupta, 1985). On a weight basis illite is most reactive and kaolinite least reactive. Chain silicate minerals such as olivine and augite adsorb more B than the micaceous layer silicates muscovite, vermiculite, and biotite. At a high pH, Al and Fe hydroxides and oxides, through ligand exchange, provide the main mechanism for bonding B (Bingham et al., 1970).
2. B complexed with organic matter: The exact mechanism of B-organic matter complex formation are not known, but some studies suggest basic acid condensation with diol groups associated with carboxylic acids.
3. Soluble B: Boron dissolved in soil solution is present as undissociated boric acid (H_3BO_3) or as soluble species $\text{B}(\text{OH})_4^-$ (which is $\text{H}_2\text{BO}_3^- + \text{H}_2\text{O}$). H_2BO_3^- is of importance in soils having a pH of 9.0 and above. Undissociated H_3BO_3 is considered the form in which most B is taken up by the plants (Bingham et al., 1970). The presence of different species of B as affected by pH is shown in Figure 15.1. The horizontal line H_3BO_3 passes through the solubility data for Swedish soils and can be designated as soil-B line, representing a mean level of approximately $10^{-5.5}$ M B. The bulk of B is taken up by plants by the mechanism of mass flow.

15.1.2. Factors Affecting Boron Availability

As brought out in the discussion so far, soils having a relatively high content of micaceous clay minerals (such as illite) and organic matter contain greater amounts of total and available B. On the other hand, coarse, well-drained, low-organic-matter, sandy soils usually have less total and available B.

Soil pH and liming; interactions with Ca, K, and other nutrients; and weather factors influence B availability to plants.

15.1.2.1. Soil pH and Liming

Liming strongly acidic soils frequently induces at least a temporary B deficiency in susceptible plants, which is believed to be caused by increased

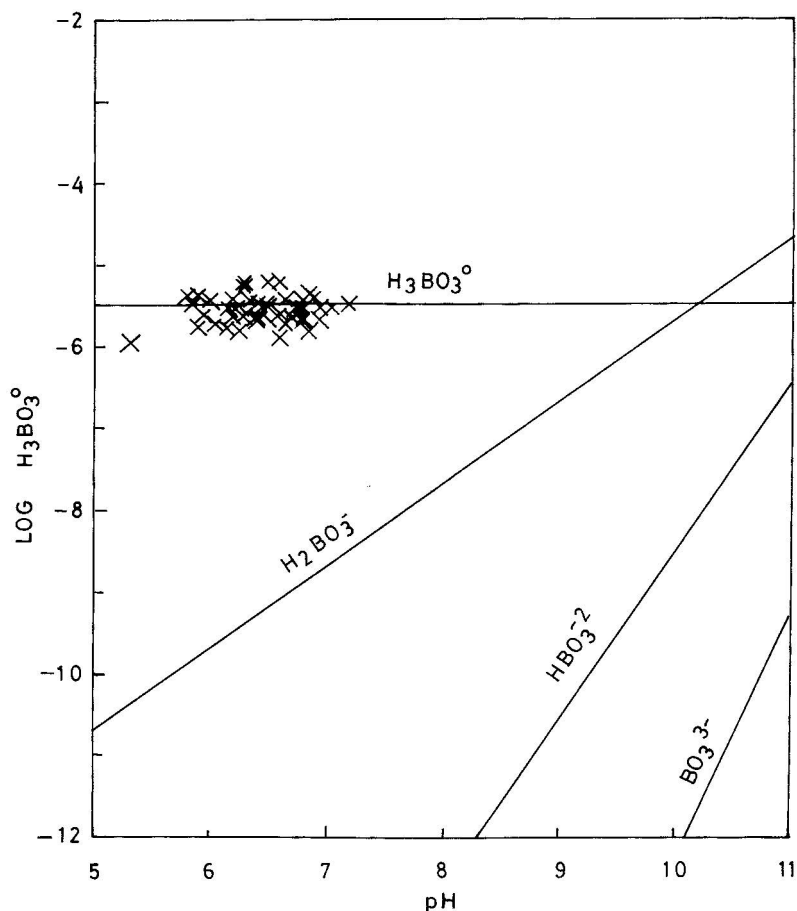


Figure 15.1. Boron species in solution, drawn to reflect equilibrium with the average soluble-B levels in 49 soils in Sweden. (From Lindsay, 1991. *Micronutrients in Agriculture*, J.J. Mortvedt, Ed., p. 107. With permission of SSSA.)

adsorption of B on freshly formed $\text{Al}(\text{OH})_3$ (Tisdale et al., 1985). As a corollary, moderate liming can be used as a corrective treatment on soils containing excess B.

15.1.2.2. Interactions with Other Nutrients

The most well known of the B interactions with other nutrients is that with Ca, as seen in liming. This effect is probably related to the Ca:B ratio in plants. For example Ca:B ratios of 10 to 45 were toxic to barley, a ratio of 180 was optimal, and ratios greater than 697 may produce B deficiency.

However, Gupta and MacLeod (1981) using CaCO_3 and CaSO_4 as sources of Ca, suggested that reduced B concentration in plants was a pH rather than a direct Ca effect.

High levels of K accentuate B deficiency, as well as toxicity symptoms, mainly by affecting Ca concentration. For example, Patel (1967) showed that B deficiency symptoms of tobacco increased and toxicity symptoms decreased with increasing Ca:B and K:B ratios.

Liberal N applications decrease the severity of B toxicity symptoms in citrus and in cereals (Gupta, 1985).

15.1.2.3. Environmental Factors

Environmental factors can influence B availability to plants. For example, in areas of adequate precipitation, B deficiency is observed only in dry seasons or in late summer when water availability is low. Plants can tolerate higher B concentrations, without experiencing harmful effects, during cool weather than during warm, humid conditions (Eaton, 1935). B toxicity can be exacerbated by high light intensity.

15.1.3. Soil Tests for Boron

The most widely used soil test for B is the hot water extraction method as proposed by Berger and Truog (1939). Other methods, including variations in the hot water extraction (Gupta, 1993a), are 0.05 M HCl, 0.01 M CaCl_2 + 0.5 M Mannitol, hot 0.02 M CaCl_2 , and Morgan's reagent.

The boron requirement for most crops is usually met when soil contains 0.5 to 1.0 mg kg^{-1} of hot water-soluble B, and levels above 5 mg kg^{-1} are likely to be toxic (Ponnamperuma et al., 1981). Deficiency, sufficiency, and toxic B levels in crop tissues are given in [Table 15.1](#). In general, crucifers and legumes have a much greater need for B than the cereals. Nevertheless, large differences exist between cultivars of the same species in respect to B requirements.

15.1.4. Boron Deficiency Symptoms in Plants

Boron plays an essential role in the development and growth of new cells in the meristematic tissue and imparts stability to the pollen tubes. It is also involved in the germination and growth of pollen. Boron also facilitates the translocation of sugar through the phloem.

Boron is one of the least mobile of the micronutrients in plants and is not readily translocated from old to young plant parts. The first symptoms of B deficiency therefore appear in the growing points and meristematic tissue—the stem tips, root tips, new leaves, and flower buds. Boron deficiency symptoms include thickened, cracked, and wilted leaves, petioles, and stems, as well as

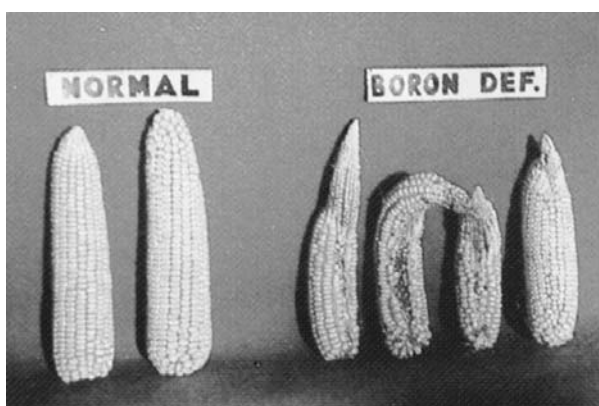
Table 15.1 Deficiency, Sufficiency, and Toxicity Levels of Boron on Crops

Crop	Part of plant tissue sampled	Deficient	Sufficient	Toxic
		mg B kg ⁻¹ dry matter		
A. Crops responsive to B application; may tolerate high B levels				
Alfalfa (<i>Medicago sativa</i> L.)	Whole tops at early bloom	<15	20–40	200
Snap beans (<i>Phaseolus vulgaris</i> L.)	Whole tops at early bloom stage	<12	42	>125
Birdsfoot trefoil (<i>Lotus comiculatus</i> L.)	Whole tops at bud stage	14	30–45	>68
Brussel sprouts (<i>Brassica oleracea</i> var. <i>gemmifera</i> Zenker)	Leaf tissue when sprouts begin to form	6–10	13–101	—
Carrots (<i>Daucus carota</i> L.)	Mature leaf lamina	<16	32–103	175–307
Celery (<i>Apium graveolens</i> L.)	Leaflets	20	68–432	720
Cucumber (<i>Cucumis sativus</i> L.)	Mature leaves from center of stems 2 weeks after first picking	<20	40–120	>300
Red clover (<i>Trifolium pratens</i> L.)	Whole tops at bud stage	12–20	21–45	>59
Rutabaga (<i>Brassica napobrassica</i> , Mill)	Leaf tissue at harvest	20–38	38–140	>250
Sugarbeets (<i>Beta vulgaris</i> L.)	Middle fully developed leaf without stem taken at end of June/early July	<20	31–200	>800
Tomatoes (<i>Lycopersicon eselentum</i> Mill)	Mature young leaves from top of 63-day-old plants	<10	30–75	>200
Spanish peanuts (<i>Arachis hypogea</i> L.)	Young leaf tissue from 30-day-old plants	—	54–65	>250

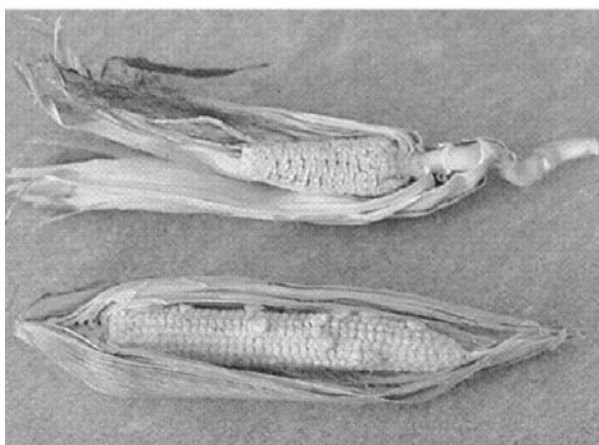
Table 15.1 Deficiency, Sufficiency, and Toxicity Levels of Boron on Crops (Continued)

Crop	Part of plant tissue sampled	Deficient	Sufficient	Toxic
		mg B kg ⁻¹ dry matter		
B. Crops less responsive to B application; less tolerant to high B levels				
Corn (<i>Zea mays</i> L.)	Total above-ground plant material at vegetative stage until ear formation	<9	15–90	>100
Oats (<i>Avena sativa</i> L.)	Boot stage tissue	3.5–5.6	14–24	>50
Soybean (<i>Glycine max</i>)	Mature trifoliolate leaves at early bloom	9–10	—	63
Barley (<i>Hordeum vulgare</i> L.)	Boot stage tissue	7.1–8.6	21	>46
Wheat (<i>Triticum aestivum</i> L.)	Boot stage tissue	2.1–5.0	8	>16

Adapted from Gupta (1993b).



A



B

Figure 15.2. Boron deficiency symptoms. (A) Twisted, deformed ears with many rows missing and poorly filled kernels. (B) Deformed ears with very few kernels forming. (From *Corn Field Manual*, J.R. Simplot Company Minerals & Chemistry Division, Pocatello, ID, ©1984. With permission.) See Plate 10.

discoloration, cracking, or rotting of fruits, tubers, or roots (Figure 15.2). In cotton square or boll shedding may take place due to B deficiency.

15.1.5. Boron Fertilizers

Boron is applied to both soils and foliage. When applied to soil, B-fertilizers should be uniformly banded or broadcast and incorporated into the

Table 15.2 Commonly Used Boron Fertilizers

Fertilizer	Chemical formula	B content (%)
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	11
Boric acid	H_3BO_3	17
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	10–18
Sodium tetraborate		
Fertilizer borate 68	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	14–15
Fertilizer borate 68	$\text{Na}_2\text{B}_4\text{O}_7$	21
Solubor	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 15\text{H}_2\text{O} +$ $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$	20–21
Boron frits	Complex borosilicates	2–11

From Tisdale et al. 1993. *Soil Fertility and Fertilizers*, 5th ed., p. 342.

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soil. Foliar application of B is practiced in orchards and also in field crops such as cotton, which need insecticidal sprays; B can be easily mixed with insecticides. The method of application has an important bearing on the rate at which B is applied. A dose of 0.5 to 1 kg B ha⁻¹ is recommended for soil application; it may be increased when B is broadcast. For foliar application a dose of 0.1 to 0.5 kg ha⁻¹ is generally recommended. Some commonly used B fertilizers are listed in Table 15.2

15.2. MOLYBDENUM

Molybdenum content in soils ranges from 0.2 to 5 mg kg⁻¹ and averages about 2 mg kg⁻¹ (Tisdale et al., 1985). The essentiality of Mo was established by Arnon and Stout (1939), while its role in N₂-fixation by *Azotobacter chroococcum* was reported by Bortels (1930). Mulder (1948) showed that Mo was also essential for symbiotic N₂-fixation by *Rhizobium*.

For field crops, response to Mo application was first reported by Anderson (1942) who applied 1 kg ha⁻¹ ammonium molybdate to subterranean clover (*Trifolium subterraneum* L.)–perennial rye grass (*Lolium perenne* L.)–*Phalaris aquatica* L. pastures in South Australia. Molybdenum then became an essential component of fertilization packages in Australia. Response of wheat and oats to Mo was later reported from Western Australia (Gartell, 1966). Responses of crops to Mo are closely related to soil properties, and, consequently, there are established geographical patterns of deficiency and of excess. Large areas of North America, Australia, New Zealand, and probably eastern Europe are potentially deficient in Mo (Gupta and Lipsett, 1981). Mo deficiency is expected on well-drained, leached-acid soils and on some sandy soils. In the United States, responses to Mo have been obtained in the Atlantic and Gulf coasts, California, the Pacific Northwest, Nebraska, and the states bordering the Great Lakes.

It may be pointed out that Mo is needed in very small amounts (a few mg ha⁻¹), and often seed reserves of Mo are sufficient to take care of the crop needs. For example, Weir and Hudson (1966) observed that Mo deficiency symptoms in maize were unlikely even in low-Mo soils when the Mo content in seed was >0.08 mg kg⁻¹, but were likely for seed Mo concentrations of <0.02 mg kg⁻¹.

15.2.1. Forms of Molybdenum in Soils

Like any other nutrient, Mo in soils is present in the crystal lattice of primary and secondary minerals, is bound to Al and Fe hydroxides and oxides, complexed with soil organic matter, held as an exchangeable anion, and dissolved in soil solution.

In soil solution Mo is present the following ionic species: MoO₄²⁻, HMoO₄⁻, and H₂MoO₄⁰. The concentration of these three species is highly pH dependent. As can be seen in [Figure 15.3](#), MoO₄²⁻ is the most prevalent species, followed by HMoO₄⁻. The availability (solubility) of both these species and thus of Mo increases with pH. At pH 6.5 the concentration of MoO₄²⁻ is 10^{-7.5} M. The concentration of Mo in soil solution is generally 2 to 8 mg Mg⁻¹ (2 parts per billion). When the concentration is less than 4 mg Mg⁻¹, diffusion is the main mechanism of Mo uptake by plants. When the concentration exceeds 4 mg Mg⁻¹, considerable Mo is transported to plant roots by mass flow.

15.2.2. Factors Affecting Molybdenum Availability in Soils

Soil pH, content of Fe and Al hydroxides and oxides, interaction with other ions in soil solution, and environmental factors affect Mo availability in soils.

15.2.2.1. Soil pH and Liming

The effect of pH on the increased availability of MoO₄²⁻ and HMoO₄⁻ ions has already been discussed. The general relationship between soil particles, Mo, and pH can be written as follows:



Thus, in general, there is a tenfold increase in MoO₄²⁻ for each unit increase in soil pH.

Liming will improve Mo availability because pH is increased. On the other hand, acid-forming fertilizers such as ammonium sulfate are likely to decrease Mo availability. Large and continuous application of such fertilizers will increase Mo deficiency.

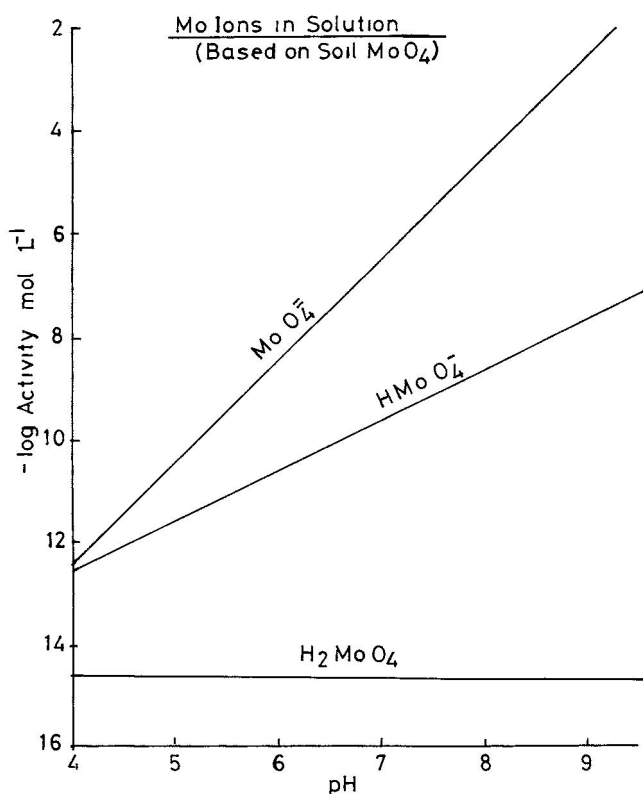


Figure 15.3. Solution species of molybdenum shown in equilibrium with soil-Mo, which has a value of $10^{-7.5} \text{ M}$ at pH 6.5. (From Lindsay, 1991. *Micronutrients in Agriculture*, J.J. Mortvedt, Ed., p. 110. With permission of SSSA.)

15.2.2.2. Effects of Fe and Al Oxides

Fe oxides (and Al oxides to a lesser degree) can sorb large quantities of MoO_4^{2-} , particularly under acidic conditions when these oxides acquire a positive charge. For example, in a study by Jones (1956) adsorption of Mo by Fe_2O_3 in a solution containing 100 mg Mo decreased from 98 μg at pH 7 to 22 μg at pH 9 after shaking with 100 mg of amorphous Fe_2O_3 . Similarly, the adsorption maximum of MoO_4^{2-} on hematite was reduced by 80% if pH was changed from 4 to 7.75 (Reyes and Jurinak, 1967).

15.2.2.3. Interaction with Other Ions in Soil Solution

Of the anions, phosphate increases and sulfate decreases Mo uptake by plants. The increase in Mo uptake by plants due to phosphate may result from

increased release of adsorbed MoO_4^{2-} or from the formation of a complex phosphomolybdate ion, which is more soluble and adsorbed more readily by plants (Barshad, 1951). The inhibitory antagonistic effects of SO_4^{2-} on Mo content have been suggested to occur primarily during the absorption process, with some antagonistic mechanism involved during translocation from roots to shoots (Gupta and Lipsett, 1981).

Of the cations, Mg has been reported to increase Mo uptake, while Cu and Mn have antagonistic effects (Tisdale, et al., 1985).

15.2.2.4. Environmental Effects

Molybdenum deficiency is more severe under dry weather conditions, which reduce soil water content and reduce the mobility of Mo in soil solution.

15.2.3. Soil Test for Molybdenum

The acid ammonium oxalate (AAO) procedure proposed by Grigg (1953) is the most commonly used soil extractant for Mo, and a level of $>0.2 \text{ mg kg}^{-1}$ AAO extractable Mo is identified as adequate. The other extractants proposed are ammonium acetate-EDTA and $1 \text{ M } (\text{NH}_4)_2 \text{CO}_3$ at pH 9.0 for alkaline soils. Anion-exchange resin (Dowex I \times 4) has also been suggested as an extractant for Mo. None of these reactants has been very successful in predicting Mo needs of soils or in predicting the response of crops to Mo.

15.2.4. Molybdenum Deficiency Symptoms in Plants

The symptoms of Mo deficiency are closely related to N metabolism since most of the Mo in plants is concentrated in the nitrate reductase enzyme. Deficient plants are suffering essentially from a shortage of protein due to the failure of the initial process of nitrate reduction. These specific symptoms commonly involve deformation of leaves, as in “whiptail” of cauliflower (Figure 15.4). In wheat the symptoms are yellowing of older leaves and, in acute deficiency, the presence of empty heads. In clovers and legumes also yellowing of leaves is the most common symptom. Deficiency and sufficiency levels of Mo for some crops are given in Table 15.3.

15.2.5. Molybdenum Toxicity to Animals

Molybdenum toxicity in plants has been seldom reported and generally is not a matter of concern. However, excessive amounts of Mo (20 to 30 mg kg^{-1} dry matter) in forage can be toxic to animals feeding on such forage. This toxicity disease in animals is known as molybdenosis and is due to Mo-Cu imbalance. This disease is also known as “teart” in England and “peat scours” in New Zealand. For molybdenosis the Cu:Mo ratio in animal feeds from



Figure 15.4. Whiptail in cauliflower caused by Mo deficiency. (From Katyal, J.C. and N.S. Randhawa. 1983. *Micronutrients*, FAO Fertilizer and Plant Nutrition Bulletin 7, Food and Agriculture Organization, Rome. With permission.) See Plate 11 following p. 170.

western Canada was found to be 2, whereas in some English pastures the ratio was reported to be closer to 4 (Gupta and Lipsett, 1981). Inflicted animals have bone malformation and stunted growth. Addition of Cu to the diet can cure the disease.

Molybdenosis has been reported from western areas of the United States, western Canada, England, and New Zealand. In some instances the problem is associated with soils developed from marine shales.

15.2.6. Molybdenum Fertilizers

The commonly used Mo fertilizers are ammonium molybdate $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}\cdot 2\text{H}_2\text{O})$, containing 54% Mo; sodium molybdate $(\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O})$, containing 39% Mo; molybdenum trioxide (MoO_3 , containing 66% Mo); and molybdenum frits (1 to 30% Mo).

Molybdenum may be applied to soil or foliage or put on seed prior to sowing. Coating or soaking seeds with Mo is the easiest method and involves the least amount of Mo fertilizers. When applied to soil, the doses vary from 35 to 350 g ha⁻¹ depending on the soil and crop.

Table 15.3 Deficient and Sufficient Levels of Molybdenum in Plants

Plant	Part of plant tissue samples	Mo in dry matter (mg kg ⁻¹)	
		Deficient	Sufficient
Alfalfa (<i>Medicago sativa</i> L.)	Leaves at 10% bloom	0–26–0.28	0.34
Barley (<i>Hordeum vulgare</i> L.)	Blades 8 weeks old	—	0.03–0.07
Beans (<i>Phaseolus vulgaris</i>)	Tops 8 weeks old	—	0.4
Beets (<i>Beta vulgaris</i> L.)	Tops 8 weeks old	0.05	0.62
Broccoli (<i>Brassica oleracea</i> var. <i>italica</i> Plenck.)	Tops 8 weeks old	0.04	
Brussels spouts (<i>Brassica oleracea</i> var. <i>gemmifera</i> Zenker)	Whole plants when sprouts begin to form	<0.08	0.16
Cabbage (<i>Brassica oleracea</i> var. <i>capitata</i> L.)	Above-ground portion of plants at appearance of a curd	<0.26	0.68–1.49
Cauliflower (<i>Brassica oleracea</i> var. <i>botrytis</i> L.)	Whole plants before the appearance of curd	<0.11	0.56
Corn (<i>Zea mays</i> L.)	At tassel, middle of first leaf opposite and below the lower ear	<0.1	>0.2
Lettuce (<i>Lactuca sativa</i> L.)	Leaves	0.06	0.08–0.14
Pasture grass (<i>Graminae</i>)	First cut at first bloom	—	0.2–0.7
Red clover (<i>Trifolium pratense</i> L.)	Total above-ground plants at bloom	<0.15	0.3–1.59
	Whole plants at bud stage	0.1–0.2	0.45

Table 15.3 Deficient and Sufficient Levels of Molybdenum in Plants (Continued)

Plant	Part of plant tissue samples	Mo in dry matter (mg kg ⁻¹)	
		Deficient	Sufficient
Spinach (<i>Spinacea oleracea</i> L.)	Whole tops at normal maturity	—	0.15–1.09
Sugar beets (<i>Beta vulgaris</i> L.)	Blades shortly after symptoms appear	0.01–0.15	0.2–20.0
Temperate pasture legumes	Plant shoots	—	>0.1
Timothy (<i>Phleum pratense</i> L.)	Whole tops at prebloom, head fully emerged from the panicle	0.11	—
Soybeans	Plants when 26–28 cm high	0.19	—
Tobacco (<i>Nicotiana tabacum</i> L.)	Leaves 8 weeks old	—	1.08
Tomatoes (<i>Lycopersicon esculentum</i> Mill)	Leaves 8 weeks old	0.13	0.68
Tropical pasture legumes in mixture with (<i>Panicum maximum</i> cv Gatton)	Plant shoots	—	>0.02
Wheat (<i>Triticum aestivum</i> L.)	Whole tops at boot stage	—	0.09–0.18
	Grain	—	0.16–0.20

Adapted from Gupta and Lipsett (1981).

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